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Bottari, Giovanni; Barta, Katalin

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Mini-review

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Giovanni Bottari, Katalin Barta*

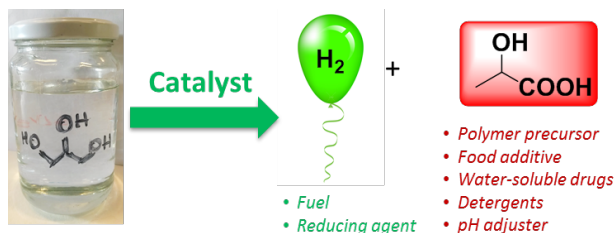
Lactic acid and hydrogen from glycerol via acceptorless dehydrogenation using homogeneous catalysts

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Abstract: Acceptorless dehydrogenation of alcohols has emerged as a powerful methodology for the valorization of biomass derived platform chemicals and building blocks. In this review we provide a short overview of the advantages and possible product outcomes of this method. The main focus will be devoted to the conversion of glycerol, which is the major waste product of biodiesel production, to lactic acid. While extensive research addresses the development of heterogeneous catalysts, recently new and highly active iridium and ruthenium complexes have also been reported. These novel homogeneous catalysts are even more active than the already reported heterogeneous systems and enable the direct conversion of glycerol into lactic acid and molecular hydrogen. While the product hydrogen might be used either as fuel or as reducing agent for other processes, lactic acid is a platform chemical widely employed by the polymer, pharmaceutical and food industries. The used catalytic methodology is atom-economic, waste-free and is uniquely suited for the efficient conversion of renewable resources.

Keywords: Biomass upgrading, Acceptorless dehydrogenation, Hydrogen storage, sustainable catalysis, glycerol



***Corresponding author: Katalin Barta:** Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen (The Netherlands), E-mail: K.barta@rug.nl

Giovanni Bottari: Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen (The Netherlands)

1 Introduction

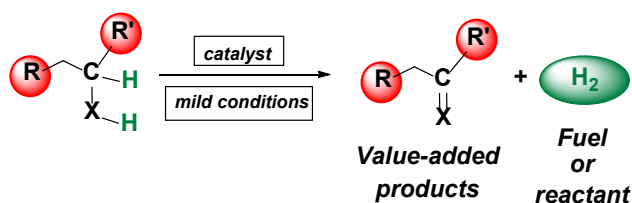
The efficient conversion of renewable resources and derived platform chemicals requires fundamentally new approaches in chemical catalysis[1-2]. While chemical pathways based on petroleum generally add functionality to simpler molecules in order to obtain value added chemicals, biomass is highly functionalized. Therefore new, efficient defunctionalization and selective bond cleavage strategies need to be considered. These new methodologies should enable the direct atom-economic and waste-free conversion of renewables in order to give access to a variety of bulk, commodity or fine chemicals. The structural diversity of biomass-derived substrates is a challenge, but also a key opportunity for the development of novel catalytic methods. Since these new methods are being designed now, it is of prime importance that sustainability aspects are considered already at the design stage, which is in accordance with the principles of green chemistry[3]. In order to access the products currently produced from petroleum, reductive as well as oxidative strategies are needed. While reduction of highly oxygenated compounds is the main methodology used for the production of biofuels at the expense of valuable hydrogen, oxidation chemistry affords functionalized products but is often associated with generating waste.

Recently, acceptorless dehydrogenation of R_2CH-XH bonds (where $X=CR_2$, NR and O) to form unsaturated $C=X$ compounds and gaseous H_2 has emerged as an attractive synthetic method[4,5]. In contrast to classical oxidation, where hydrogen equivalents are transferred from the substrate to an oxidant, in acceptorless dehydrogenation reactions these hydrogen equivalents are transferred to a transition metal complex, and the substrate is formally oxidized. Subsequently, hydrogen gas is liberated from the complex, thereby closing the catalytic cycle. Notably, this step is thermodynamically challenging and requires special design of the metal complex and careful selection

of reaction conditions. Homogeneous catalysts can effectively dehydrogenate a number of substrates in the range 90–150 °C [4,5], additionally, no waste is generated as shown in the overall reaction scheme (scheme 1). This method has two key advantages, as it simultaneously allows for:

a) The production of valuable organic compounds which are conventionally obtained by oxidation processes that generate stoichiometric amounts of waste. Such valuable compounds are olefins, ketones, aldehydes and imines. These are either final products or can be further functionalized through tandem catalytic processes, due to their inherently higher reactivity than the corresponding starting materials.

b) Production/storage of hydrogen gas. Currently, more than 90% of hydrogen is produced from fossil fuels, therefore controlled release of hydrogen from CH-XH bonds of renewables (especially alcohols) is a preferred way to access this high energy density fuel and reactant.



Scheme 1. General reaction scheme of an acceptorless dehydrogenation reaction.

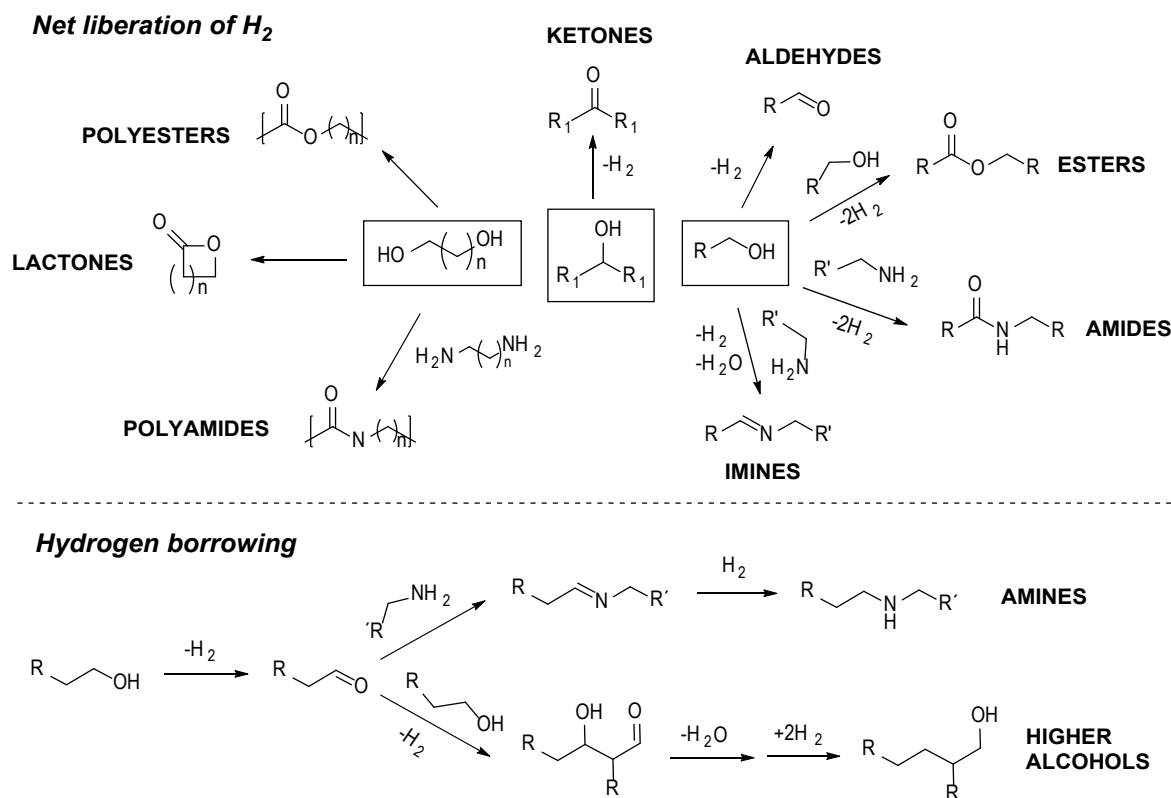
Related to point b) it is important to mention, that aqueous phase reforming (APR) of OH- containing renewable resources, mainly sugars[6,7] and glycerol[8], provides a powerful alternative for the production of hydrogen gas, that is usually performed by means of heterogeneous catalysis. The product stream may consist of alkanes as well as CO₂, depending on reaction conditions and the feed substrate. Notably, these processes require lower reaction temperatures than steam-reforming. Unique catalytic systems have also been described, where the hydrogen equivalents derived from methanol are directly used for the hydrogenolysis and hydrogenation processes required to depolymerize and reduce lignocellulosic biomass.[2]

Homogeneous catalysts have the advantage that very high activities and selectivities can be achieved through understanding of structure-activity relationships and careful design of the metal complexes. In the next section several such catalytic systems will be discussed.

2 Scope and importance of acceptorless dehydrogenation reactions

In the last two decades, catalytic dehydrogenation of several types of organic substrates into their corresponding unsaturated analogues have been studied. It was found, that poorly reactive alkanes and cycloalkanes can be successfully dehydrogenated to α -olefins and cycloalkenes, which are commodity chemicals with a tremendous range of applications. In these reactions, several robust iridium pincer complexes have been used[9]. Compared to the simple dehydrogenation of cyclohexane to benzene, the introduction of nitrogen atoms results in much more favorable thermodynamics of H₂ release from the heterocycle (e.g. pyrrolidine to pyrrole), which led to a new concept of “organic liquids” as hydrogen storage materials (HSMs)[10]. Also the dehydrogenation of alcohols has received particular attention recently, primarily due to implications in the conversion of renewables, although the first examples date back to a few decades ago[11–15]. This simple reaction is used in a wide range of chemical transformations, providing access to a variety of different products that are schematically illustrated in scheme 2. Acceptorless dehydrogenation of primary and secondary alcohols affords aldehydes and ketones, respectively. Esters and amides are formed by subsequent reactions of the carbonyl compounds with an additional equivalent of alcohol or an amine and the hemiacetal and hemiaminal intermediates are rapidly dehydrogenated with formation of total two equivalents of hydrogen. Alternatively, carbonyl compounds can react in situ with amines to form imines as final product. The same classes of reactions apply to diols, which are suitable substrates for polymerization reactions. Diols are readily available from biomass sources and, particularly, α,ω -diols[16–19] are useful precursors for lactones,[20–23] polyesters[24] and polyamides[25,26]. This green synthetic approach has evident advantages with respect to the polycondensation of diacids with diols/diamines which affords polymers with lower molecular weights and overall yields.

A closely related approach is the so called “hydrogen borrowing” strategy, during which the hydrogen equivalents borrowed from the substrate are temporarily stored at the metal complex, and instead of being released, are used for reduction of unsaturated intermediates which formed by further reactions of the oxidized substrate. For example, alcohol dehydrogenation affords more reactive carbonyl compounds which can undergo self-



Scheme 2. Product pool accessible via acceptorless hydrogenation of alcohols and diols (top) and diverse products via hydrogen borrowing methodology (bottom).

condensation reactions to form the corresponding aldol intermediates. These act as acceptors for the borrowed hydrogen equivalents to afford the Guerbet alcohols[27,28] as final product. A very important reaction is the direct amination of alcohols. Here the primary and secondary alcohol is dehydrogenated to a carbonyl compound that react with an amine to form imines which are in situ reduced to give the corresponding amines. [29-32] Similarly to the acceptorless dehydrogenation, substantial progress was made recently in the development of molecular organometallic catalysts for the conversion of alcohols via the borrowing hydrogen strategy, which will have great potential in the benign valorisation of biomass feedstocks.[33-36]

It is worth mentioning that the occurrence of the two pathways (dehydrogenative coupling and release of H_2 or hydrogen borrowing), illustrated in scheme 2 is strongly dependent on the catalytic system. For instance it was shown for a series of Ru(N-N)(P-P) complexes that in the reactions between alcohols and amines, the ligand is a crucial factor discriminating the selectivity towards either amide or amine products[37,38].

It is also worth mentioning research directions that, similar to APR procedures, are primarily targeting

the production of hydrogen gas from simple monoalcohols. Homogeneous transition metal complexes were used to generate a pure stream of H_2 and CO_2 from methanol/water mixtures. [39,40] Furthermore, ethyl acetate synthesis[41] was accomplished through ethanol dehydrogenation. Remarkably, these processes, catalyzed by robust ruthenium complexes, and operating under very mild conditions (<100 °C) when compared to methanol steam reforming[42]. Closely related to methanol dehydrogenation, the conversion of formaldehyde and paraformaldehyde to H_2 and CO_2 at mild temperature (95 °C) was reported by Pechtl and coworkers[43] by another [Ru(p-cymene)Cl₂]₂ complex; the catalytic system has proven robust under experimental conditions (presence of oxygen and water) usually detrimental for organometallic species. Polyols are interesting substrates, as multiple positions are available for accessing distinct valuable products by the dehydrogenation approach. In particular, glycerol, a triol that can be obtained in large scale from transesterification of fatty acids, provides an interesting case study for the valorization of biomass using the acceptorless dehydrogenation methodology and will be described in more detail in the following section.

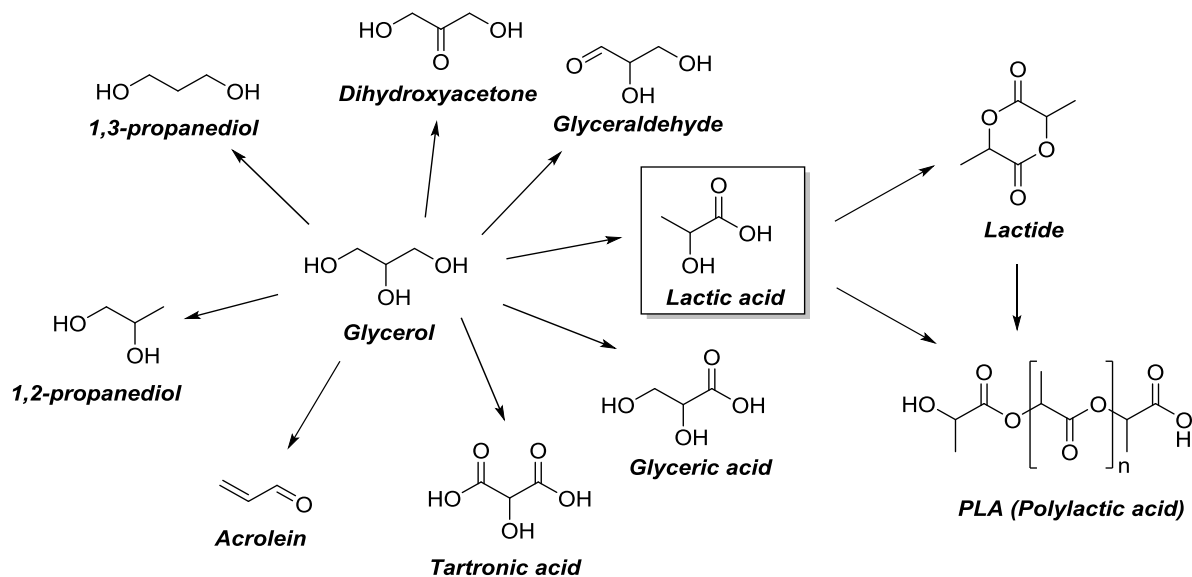
3 From glycerol to lactic acid

Efficient upgrading of glycerol is desirable since this highly viscous liquid represents 10% of the waste produced from biodiesel manufacturing[44]. Before 2005, glycerol production was <100 million gallons; remarkably, environmental policies have incentivized biodiesel production with a consequent sharp increase of crude glycerol on the market up to 450 million gallons in 2007[44]. The waste glycerol is preferably burned, despite its low heating value, notably decreasing the price of crude glycerol and creating an incentive for its efficient upgrading to valuable compounds. Propanediols[45,46] and acrolein[47] are among the most studied products from glycerol upgrading. Regarding catalytic oxidation of glycerol[48], various C3-acids, such as glyceric, tartronic and hydroxypyruvic acids can be obtained, however less attention was devoted to lactic acid, an important platform chemical which can be synthesized either by bio- or by chemo-catalysis (scheme 3). Fermentation methods have the advantage of accessing the pure L enantiomer, which is largely employed for the synthesis of L-poly lactide[49]. Chemocatalytic methods can also give access to the less available and more expensive D-lactic acid, although the racemic mixture is obtained. Biochemical processes generally suffer from low productivities and expensive product purification procedures[50]. Catalytic methods, primarily heterogeneous catalysts using oxidants, have been investigated. Platinum and ruthenium supported on carbon can catalyze the conversion of glycerol into lactic acid at 200 °C with addition of a base through an initial

dehydrogenation step; selectivities to lactate exceed 60% only at low conversion (20%)[51]. Very high lactate yields can be achieved with AuPt bimetallic catalysts supported on ceria in presence of NaOH base; up to 80% lactate yield can be obtained at mild temperature (373 K) using O_2 as oxidant[52]. Production of lactate raises issues related to generation of waste and the need for additional separation procedures. Oxidation of glycerol to lactic acid under acidic conditions would eliminate further steps. Boric acid was found to promote high selectivity to lactic acid in the presence of a $Pt/CaCO_3$ catalyst allowing for moderate selectivity (54%) at higher conversion (45%)[53]. Bimetallic AuPd catalysts supported on titania can oxidize glycerol to lactic acid with $AlCl_3$ as cocatalyst[54]. Also homogeneous acidic co-catalysts produce notable amounts of waste. Nonetheless, the use of tin zeolites coupled with a platinum catalyst for glycerol oxidation in water solutions led to lactic acid selectivities up to 80% at 90% conversion[55].

Recently, acceptorless dehydrogenation was used for the conversion of glycerol to hydrogen and lactic acid. Homogeneous catalysts were investigated to improve the low productivities typical for biochemical processes and avoid harsh conditions necessary for heterogeneous catalysts. Indeed, the highest selectivity and productivity in this reaction, even surpassing the best values obtained with heterogeneous catalysts so far, were achieved by Campos and Crabtree with iridium complexes (Figure 1) [56].

Glycerol has already been used as a solvent and hydrogen donor by activation with iridium carbenes for



Scheme 3. Routes for the upgrading of glycerol to valuable products.

reduction of ketones[57,58]. In previous reports from Crabtree and coworkers, bis(carbene)iridium complexes proved highly active in hydrogen transfer of carbonyl compounds[59-61]. This led the research group to perform a systematic screening of several iridium complexes active in the above mentioned reactions and, indeed, the presence of two N-heterocyclic carbene ligands (NHC) afforded active catalysts (complexes **1-3**, figure 1) in the target reaction.

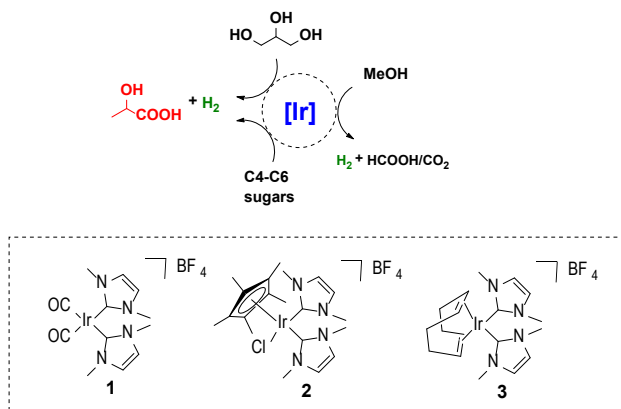
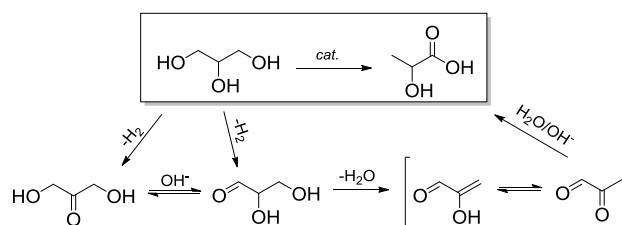


Figure 1. Iridium complexes used for conversion of glycerol to lactic acid and hydrogen and related dehydrogenation reactions.

It was demonstrated in previous studies that an interesting feature of the abovementioned complexes is that the strongly coordinating carbene ligands give rise to robust air- and moisture-stable polyhydride iridium species which are likely the active catalysts[59-60]. Very low loading of cationic iridium carbene complex **1** (0.002-0.036%) was used to achieve TON values as high as 30100 in the conversion of neat glycerol (115 °C, 90h), while compounds **2** and **3** showed slightly lower activity. Also in aqueous solutions the catalysts showed remarkable activity. Upgrading of crude glycerol is challenging due to the potential deactivation of catalysts by the impurities derived from biodiesel production.

The authors also showed that iridium complex **1** dehydrogenates crude glycerol (68% purity) to lactic acid with 96% selectivity at 98% conversion, only using 0.6 mol% catalyst loading, with no substantial change in activity with respect to pure glycerol. According to mechanistic investigations performed by the authors, glycerol would be first catalytically dehydrogenated to dihydroxyacetone (DHA)[62] or glyceraldehyde (GAL), these two being intermediates in equilibrium under basic conditions (scheme 4)[63].



Scheme 4. Catalytic production of lactic acid and hydrogen from glycerol.

Dehydration of glyceraldehyde should be fast enough to suppress competing processes due to C-C cleavage leading to C2 (ethylene glycol and glycolaldehyde) plus C1 products (methanol and formaldehyde). Base-catalyzed rehydration irreversibly favors lactate salt formation, preventing the hydrogenation of the tautomeric intermediates to 1,2-propanediol. Despite the possible formation of several by-products, selectivity to lactic acid with the reported iridium complexes surpasses 95% in a broad range of experimental conditions. Remarkably, C4-C6 sugars can be converted to lactic acid and H₂ by complex **1**, although catalyst deactivation prevents from obtaining very high LA yields[64]. A unique carbene-Ir₆ cluster was characterized and identified as major product of deactivation in glycerol dehydrogenation suggesting a minor role of other ancillary ligands in the iridium precatalyst[65]. Finally, complex **1** has been successfully applied to related methanol dehydrogenation reactions such as H₂ production through reforming to formate/carbonate, transfer hydrogenation of ketones and imines and aniline methylation[66].

Subsequently, Beller and coworkers reported on several ruthenium complexes containing pincer ligands (PNP, PNN and CNN) as efficient catalysts for lactic acid and H₂ production from glycerol[67]. Under relatively mild conditions (125 °C, 1.5 M KOH, diglyme solvent), 200 ppm of complex **4** (figure 2) afforded within 200 minutes H₂ (10%), lactic acid (12%) and 1,2-PDO (11%) as main products plus acetic acid and CO₂ as minor products. Up to 67% glycerol yield was obtained under optimized experimental conditions (140 °C, 24h, 1eq water, 1.08 eq NaOH and NMP as solvent). The same class of ruthenium complexes have been successfully applied in the already mentioned low temperature methanol reforming[34] (figure 2) as well as the dehydrogenation of other alcohols[41,68-71]. An analogous mechanistic pathway to that proposed by Crabtree et al. for lactic acid formation has been postulated. Remarkably, industrial glycerol (86-88% purity) was converted using complex

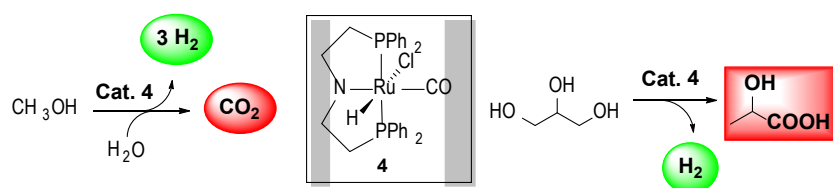


Figure 2. Ru-MACHO complex (centre) and its application to both methanol reforming and lactic acid production from glycerol.

4 with exceptionally high rates (TOF 30199 h^{-1} after only 1h), even higher than those observed for pure glycerol. Hydrogen production was observed also using ethylene glycol as substrate (TOF 64 459 h^{-1} after 1 h), however dehydrogenation of D-sorbitol only showed a TOF of 1025 (1h) using the same catalyst.

Nevertheless, the study highlights that glycerol is a useful model compound for polyol dehydrogenation, and future studies should focus on expanding the scope of ruthenium pincer and related catalysts for the conversion of mono- and poly-saccharides.

4 Conclusion

In summary, acceptorless dehydrogenation represents a powerful tool in the sustainable valorization of alcohol substrates, which are widely present, or are easy to access from renewable resources. Mono-alcohols and diols are promising biomass-derived substrates for the clean production of hydrogen and valuable organic compounds. Dehydrogenation of polyols is still a less explored field, with notable recent advances in the conversion of glycerol. In particular, iridium-carbene and ruthenium pincer complexes have proven very efficient in the acceptorless dehydrogenation of glycerol to lactic acid and hydrogen with excellent LA selectivity and TON values.

Despite the remarkable advantages of these systems, drawbacks are in the need of stoichiometric amounts of base and the cost of and scarcity of the catalyst. Ideally, these studies which provided proof of principle for highly efficient glycerol to LA transformation using transition metal complexes, will serve a basis for the development of catalysts that use more sustainable metals.

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